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"EFFECT OF WETTABILITY OF POROUS
MEDIA ON OIL RECOVERY BY WATER FLOOD"

BY

I. L. BUDHIRAJA

A THESIS

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ABSTRACT

As a result of water flood studies made on a long unconsolidated core consisting of a pack of glass spheres, it has been found that breakthrough recovery decreases by about 16 per cent as the wettability of the pack is changed from preferentially water wet to preferentially oil wet. This change in wettability has been brought about by treating the glass spheres with dilute solutions of Dri-film in benzene. The ultimate recovery has also been found to decrease as the oil wetness of the porous medium increases.

The degree of wettability of the porous medium has been estimated by carrying out contact angle measurements in glass capillary tubes. An attempt has been made to establish the same wetting conditions in the capillary tubes as in the porous medium. This has been done by keeping the ratio of the volume of the treating liquid to the surface area treated, approximately the same in both.

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INTRODUCTION

The work of many investigators has shown that the relative wettability of a rock surface has a pronounced effect on such measurements as capillary pressure, imbibition rate, relative permeability and oil recovery in water floods. Wettability is usually defined in terms of the contact angle between the fluid interface and the solid surface. However in porous media a direct measurement of contact angles is impractical if not impossible. So quite often indirect means are used to obtain some knowledge of the values of the contact angles prevailing in the porous media. Slobod and Blum; Newcombe, McGhee and Rzasa; Wagner and Leach; and Bethel and Calhoun have described some of the methods used for measuring contact angles external to the system.

Rapoport and Leas, and Geerstma, Croes and Schwartz, have carried out the dimensional analysis of the problem of flow of two immiscible and incompressible fluids through a porous medium. They have suggested the use of the scaling coefficient $\frac{6 \cos\theta \sqrt{K/\phi}}{V \mu_w L}$ to study the effect of wettability of the porous medium on oil recovery in water floods.

The primary objective of this laboratory study was to determine the effect of changes in wetting conditions of the porous media on oil recovery in water floods. These laboratory floods were carried out on an unconsolidated porous pack made of glass spheres 61 - 104 microns in size. The wetting conditions of this pack were varied by successively treating it with organosilicone solutions of increasing strength. Physical properties of the

porous pack, such as permeability, porosity, and pore geometry which might have considerable influence on the flow behaviour of the porous medium were thus held constant.

Contact angle measurements were made external to the system— on glass capillary tubes. An attempt was made to establish the same surface treatment on these glass capillaries as the porous medium.

Water flood results compare quite favourably with the results obtained earlier by several workers. An attempt has been made to explain these results on the basis of existing theory.

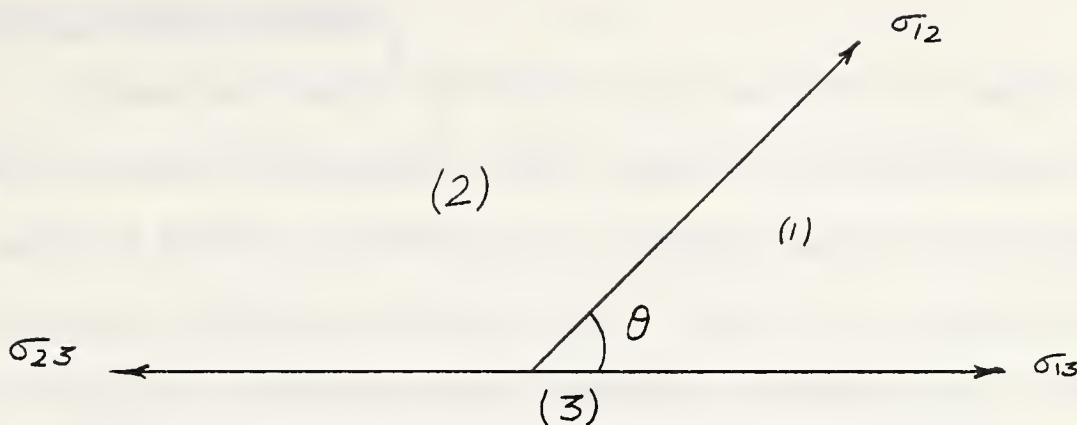
THEORY

1. WETTABILITY

Wetting can be defined as the process in which one fluid phase is displaced, completely or in part, by another fluid phase from the surface of a solid, all three phases being co-existent. The term "preferential wettability" as it is applied to a rock surface, and the liquid phases--water and oil--may be defined qualitatively by considering the behaviour of water and oil when they are placed in contact on the rock surface. Thus if the water tends to displace oil from the rock surface, the rock will be termed preferentially water wet. Similarly if oil tends to displace water, the rock will be termed preferentially oil wet.

The degree of wettability is measured by the contact angle for the system solid-water-oil. The contact angle measured in a liquid, say water, on the surface of a solid in the presence of another liquid, say oil, is invariably greater if the position of equilibrium has been reached by water advancing across the solid, rather than by the reverse process. The former is called the advancing contact angle and the latter is called the receding contact angle. The difference is due to the existence of the so called "hysteresis effect."

There are several possible explanations for the hysteresis effect. The classical one is that the orientation of the surface atoms, ions or molecules in a solid is affected by its previous history. If for example, fluid 1 in the figure to follow is water, and fluid 2 is oil, then



it is postulated that if the surface has been in contact with water so that water is the receding phase, then the surface contains more hydrophylic groups than it does if water is advancing over a surface which has been in contact with air or oil.

An alternate explanation is that hysteresis is due to surface roughness, so that an advancing meniscus represents the wetting of a surface which is (at least momentarily) a composite one. A composite surface is formed as the result of porosity. In this case the pores in the solid-water interface remain filled with oil, so that the apparent solid-water interface, is in reality a composite interface containing an area of true solid-water interface and an area of oil-solid interface. It has been shown that simple roughness (as distinct from compositeness) can explain hysteresis on the grounds of distortion of menisci by the contortion energy. Contortion energy is the energy needed to distort a liquid interface as it passes over an edge or a convex surface.

A water wet system is defined as one in which the advancing contact angle is less than 90° . An oil wet system is defined as one in which the advancing contact angle for water is greater than 90° .

EFFECT of SURFACE ROUGHNESS

⁴ Cassie and Baxter have treated the case of rough surface formed as a result of porosity. They point out that when the true contact angle is finite, the effect of a surface roughness which leads to the formation of composite surface, will always be to increase the contact angle. This of course means that the work of adhesion will always be decreased, which means that oil will be less readily displaced by the water (in the case of preferentially water wet systems) from the rough surface than if the surface were substantially smooth.

The surface forces in a solid-water-oil system are related by Young - Dupre ²² equation as follows:

$$A_{sw} - A_{so} = \sigma_{so} - \sigma_{sw} = \sigma_{ow} \cos\theta = -\Delta F$$

Where $A_{(sw)}$ = adhesion tension between solid and water,

$A_{(so)}$ = adhesion tension between solid and oil

ΔF = free energy of displacement of oil by water from a solid surface,

$\sigma_{(so)}$ = interfacial tension between solid and oil, dynes/cm.

$\sigma_{(sw)}$ = interfacial tension between solid and water, dynes/cm.

$\sigma_{(ow)}$ = interfacial tension between oil and water, dynes/cm.

These surface forces are commonly expressed as the difference in adhesion tension, or the product of water oil interfacial tension and the contact angle. If the contact angle is less than 90°, the adhesion tension difference is positive and the oil displacement by water from a solid surface will be spontaneous and favoured by a high water oil interfacial tension.

The term $\sigma \cos \theta$ has the dimensions of energy per unit of surface and can be considered as the work which corresponds to wetting by the advancing phase of the unit of surface of solid substance, previously wet with oil. This work is positive when energy is gained during wetting. Thus the greater the gain in the specific wetting work, the more completely is oil displaced. If the angle is greater than 90° , the displacement will not be spontaneous but will require less energy the lower the interfacial tension.

2. DIMENSIONAL ANALYSIS

The purpose of the dimensional analysis of a problem is to reduce the number of variables in the problem. This reduction is carried out by arranging all the variables, in a set of dimensionless groups. This considerably reduces the experimental work required to determine any particular function.

The application of dimensional analysis to a particular problem is based on the hypothesis that the solution of the problem is expressible by means of a dimensionally homogeneous equation in terms of specified variables. This hypothesis is justified by the fact that the fundamental equation of physics (such as fluid flow equations) are dimensionally homogeneous and the relationships that are deducible from these equations are consequently dimensionally homogeneous.

The first step in the dimensional analysis of this problem is to decide what variables enter the problem. If variables are introduced that really do not affect the phenomenon, too many terms may appear in the final equation. If variables are omitted,

that logically may influence the phenomenon, the calculation may reach an impasse, but more often, they lead to an incomplete or erroneous result. Even though some variables are practically constant (eg. acceleration of gravity) they may be essential because they combine with other active variables to form dimensionless products.

One must however understand the physical phenomenon in the problem being undertaken, and know enough about the problem to know why and how the variables influence the problem.

If the differential equations that govern the phenomenon are available, they show directly which variables are significant.

Innumerable dimensionless groups or products can be formed from a given number of variables. The number of dimensionless products which are sufficient to completely define a system is given by Buckingham π -Theorem; which can be stated as follows:

"Total number of dimensionless groups in a complete set
is equal to the total number of variables minus the number
of fundamental dimensions."

The Buckingham π -theorem does not give any indication as to which of the various dimensionless products available are pertinent to the problem. A knowledge of the physics of the phenomenon under study is essential to choose the pertinent groups, and if such knowledge does not exist experimental study has to be undertaken to discard the superfluous groups.

The continuity equations for the flow of two immiscible liquids

(oil and water) in a porous medium are respectively

$$\text{For the oil phase} \quad \sum_{i=1}^3 \frac{\partial}{\partial x_i} (\rho_o \vec{V}_o) = - \frac{\partial}{\partial t} (\rho_o \phi s_o) \quad * \quad (1)$$

$$\text{For the water phase} \quad \sum_{i=1}^3 \frac{\partial}{\partial x_i} (\rho_w \vec{V}_w) = - \frac{\partial}{\partial t} (\rho_w \phi s_w) \quad (2)$$

If the pore space is completely filled with these two liquids

$$s_o + s_w = 1 \quad (3)$$

The generalised Darcy equations for the simultaneous flow of oil and water may be written

$$\text{As } \vec{V}_o = \sum_{i=1}^3 - \frac{Kk_{ro}}{\mu_o} \cdot \frac{\partial \pi_o}{\partial x_i}$$

$$\text{And } \vec{V}_w = \sum_{i=1}^3 - \frac{Kk_{rw}}{\mu_w} \cdot \frac{\partial \pi_w}{\partial x_i}$$

Where π_o and π_w are the flow potentials of oil and water phases respectively, and are given as follows:

$$\pi_o = p_o + \rho_o g x_3 \quad (6)$$

$$\pi_w = p_w + \rho_w g x_3 \quad (7)$$

The pressures in the two fluids are related through the capillary pressure by

$$\begin{aligned} p_c &= p_w - p_o \\ &= \sigma \cos \theta \cdot J(s_w) \sqrt{\phi / k} \quad \text{where } J(s_w) \\ &\quad \text{is the Leverett's 'J' function}^{12} \end{aligned}$$

* See definitions of terms in nomenclature.

If we now reduce the problem to a one dimensional horizontal system, then the following 16 variables are simultaneously involved in it.

$L, t, \phi, K, \mu_o, \mu_w, \rho_o, \rho_w, g, \sigma, \theta, J(S_w), k_{rw}, k_{ro}, S_w, V, \text{ or } P$, where L is the length of the system.

We also find that, σ, θ , and ϕ always occur together as $\sigma \cos \theta \sqrt{\phi}$, so $\sigma \cos \theta \sqrt{\phi}$ can be treated as a single variable. This reduces the number of variables to 14, and according to Buckingham π -Theorem, the number of dimensionless groups in a complete set to define the system must be $14 - 3 = 11$.

The following eleven dimensionless groups can be arrived at after a complete dimensional analysis:

$$\frac{\mu_o}{\mu_w}, \frac{\rho_o}{\rho_w}, \frac{Kt \rho_w g}{\mu_w L}, \frac{t \sigma \cos \theta \sqrt{K/\phi}}{\mu_w L^2},$$

$$\frac{dJ(S_w)}{dS_w}, k_{rw}, k_{ro}, S_w, \frac{L}{\sqrt{K}}, \frac{\rho_w L \sqrt{K}}{t \mu_w},$$

and either $\frac{Vt}{L}$, or $\frac{K \Delta p t}{\mu_w L^2}$

Also $t = \frac{L}{V}$, when the velocity of the displacing fluid is given.

DISCUSSION OF THE SIGNIFICANCE OF VARIOUS GROUPS

The terms $\frac{\mu_o}{\mu_w}, \frac{\rho_o}{\rho_w}$ the ratios of the viscosities and densities respectively of oil and water, must be the same in all the floods

(or in a model and its prototype). Craig et al⁵ have used mobility ratios instead of the viscosity ratios as their scaling criterion. According to them, for water displacing oil:

$$\frac{K_{rw}/\mu_w}{K_{ro}/\mu_o} = M, \text{ should be the same for the systems being studied.}$$

This term expresses the relative ability of the displacing fluid to move behind the flood front, to the ability of the oil to flow ahead of the front.

2. The group $\frac{kt \rho_w g}{\mu_w L}$, can be written as $\frac{k \rho_w g}{\mu_w V}$, since $t = \frac{L}{V}$. Again it is convenient to write the group $\frac{K \rho_w g}{\mu_w V}$ as $\frac{K \Delta \rho g_w}{\mu_w V}$, because then the interaction that probably exists between $\frac{\rho_o}{\rho_w}$ and $\frac{K \rho_w g}{\mu_w V}$ is removed.

The meaning of the group $\frac{K \Delta \rho}{\mu_w V} g$ is very simple. It is the ratio of the hydrostatic pressure gradient, $\Delta \rho g$, and the flow potential $\frac{V \mu_w}{K}$ in the water phase.

3. The next group $\frac{t \epsilon \cos \theta \sqrt{K/\phi}}{\mu_w L^2}$ reduces to $\frac{\epsilon \cos \theta \sqrt{K/\phi}}{V \mu_w L}$

on the substitution of $t = \frac{V}{L}$.

This group gives the ratio of capillary forces to viscous forces.

4. The scaling criteria pertaining to the next four groups, namely

$\frac{dJ(S_w)}{dS_w}$, K_{ro} , K_{rw} and S_w , require that the capillary pressure and

relative permeability functions of saturation in the two systems being compared, and also the initial saturation distribution should be the same in both.

In addition to saturation, the groups $\frac{dJ(S_w)}{dS_w}$, K_{ro} , K_{rw} are

determined by pore size distribution and other physical characteristics of the rocks, and more or less by the remaining similarity groups.

5. The dimensionless groups $\frac{V_t}{L}$ or $\frac{\Delta p K}{V \mu_w L}$ are dependent groups.

They are automatically scaled if other scaling criteria are met.

6. The dimensionless group $\frac{V \rho_w K}{\mu_w}$ corresponds to Reynold's

number. If inertial forces can be neglected (as will be the case of fluid flow which is governed by the Darcy's Law), this group can be dropped.

7. The last group namely $\frac{L}{\sqrt{K}}$, gives the ratio of linear dimension of the system, to some linear dimension of the pore. It is plausible to assume that the influence of $\frac{L}{\sqrt{K}}$ can be neglected if this typical linear

dimension of the pores is much smaller than the smallest dimension in the system, i.e., if $\frac{L}{\sqrt{K}}$ is very large. The value of this group down to which this assumption is permissible has to be found experimentally.

VISCOUS FINGERING

When oil is displaced from a porous medium by water having a viscosity lower than the oil, the oil water interface is essentially unstable, and has the tendency to break up into what are called "fingers" or "streamers".

6

Viscous fingering has been studied by Engelberts and Klinkenberg and by Van
 Meurs and der Poel.¹⁹

15

Recently Outmans has given a "non-linear" theory of viscous fingering. He has given two dimensionless groups, whose values should be the same, for the systems being compared, if viscous fingering is to be properly scaled.

These groups are as follows:

$$1. \quad \left[\frac{L}{\frac{M-1}{M+1} \cdot V^* T} \right]_{\text{Syst. I}} \approx \left[\frac{L}{\frac{M-1}{M+1} \cdot V^* T} \right]_{\text{Syst. II}}$$

$$2. \quad \left[\frac{V^* L^2 (1/\lambda'_2 - 1/\lambda'_1)}{T_e} \right]_{\text{Syst. I}} \approx \left[\frac{V^* L^2 (1/\lambda'_2 - 1/\lambda'_1)}{T_e} \right]_{\text{Syst. II}}$$

When M = mobility ratio

$$V^* = V + V_c$$

V = velocity of the undisturbed interface

$$\begin{aligned} V_c &= \text{critical velocity} \\ &\approx \frac{(\rho_2 - \rho_1)g}{\frac{1}{\lambda'_2} - \frac{1}{\lambda'_1}} \end{aligned}$$

λ = mobility

$$\lambda' = \frac{\lambda}{\phi S}$$

T_e = effective interfacial tension as defined by Outmans

ϕ = porosity

S = saturation

t = time

REALISATION OF SCALING LAWS

In the experimental study undertaken, the geometrical and physical properties of the porous system such as length, diameter, porosity, permeability, and pore geometry have been held constant. The same pair of fluids was used and the rate of water injection was held constant in each flood. The initial oil saturation was maintained at 100 per cent of the pore space in all the floods.

In this way the equality of the following dimensionless groups could be realized in practice:

$$\frac{\mu_o}{\mu_w}, \quad \frac{\rho_o}{\rho_w}, \quad \frac{K \Delta \rho g}{\mu_w V}, \quad \frac{Vt}{L}, \quad \frac{V \rho_w \sqrt{K}}{\mu_w} \quad \frac{L}{\sqrt{K}} \quad \text{and } S_w$$

The equality of the remaining three groups namely $\frac{dJ(S_w)}{dS_w}$, k_{rw} and k_{ro} cannot be realized, since these groups are functions of the wetting conditions of the porous medium.

As the rate of water injection and the interfacial tension between water and oil were held constant, the two requirements for scaling the

phenomenon of viscous fingering were also met.

SURFACE TREATMENT

The experimental work involved the treatment of glass surfaces with General Electric Dri-film SC - 87. It is a clear, water white, polymeric silicone fluid containing some unhydrolyzed chlorine-silicon bonds. When applied to glass or quartz surfaces, it forms a tightly bonded, microscopically thin, water repellent film.

Silicon does not exist as such in nature but is produced from quartz or other sources of silica. This *element* is the starting point for the organosilicone monomers and polymers produced in the silicon industry. Four kinds of groups may be attached to the four valences of silicon - (1) stable, relatively unreactive organic groups such as methyl or phenyl; (2) reactive organic groups such as vinyl or beta-cyanoethyl; (3) reactive groups such as alkoxy or hydroxy; (4) atoms such as hydrogen or chlorine. The third and fourth type reactive groups or atoms provide what is called silicon-functionality, or ready reactivity at the silicon atom.

In the production of methylchlorosilanes the reaction proceeds as follows:

$\text{CH}_3\text{Cl} + \text{Si} \xrightarrow{\text{Cu}} \text{CH}_3\text{SiCl}_3 + (\text{CH}_3)_2\text{SiCl}_2 + (\text{CH}_3)_3\text{SiCl}$, plus small amounts of other products. The three reaction products listed above illustrate three types of silicone functionality available (mono-, di-, and tri-). Trimethylchlorosilane, for example, is monofunctional. It reacts with water to form a dimer.



It also reacts with surfaces to impart properties such as water repellency; or it can be used to make an end blocking unit for polymers.

Dimethyldichlorosilane is difunctional. It reacts with water to form straight chain or cyclic polymers.



It may serve as a surface treatment retaining an additional reactive site for surface or polymerisation reactions.

Methyltrichlorosilane is trifunctional and reacts with water to form cross-linked polymers.



It may be used for surface treatment retaining two sites for additional surface or polymerisation reactions.

5. THE EFFECT OF RATE ON RECOVERY

⁹ Haan has shown that at low displacement rates the capillary forces cause the formation of immobile oil pockets even in relatively homogenous water wet packs. At higher displacement rates, these capillary forces become less important causing a reduction in the size of these oil pockets, and ultimately reducing them to pore dimensions. As the rate is further increased, the occurrence of viscous fingers causes a decrease in recovery. Thus the maximum recovery will be obtained at a rate which is high enough for the capillary forces to become negligible, but is still lower than the rate at which the formation of viscous fingers starts.

In the experimental study undertaken here all the floods were made at a rate at which the maximum break-through recovery of oil was obtained for a water wet system.

LITERATURE SURVEY

1. MEASUREMENT of WETTABILITY

The degree of wettability, in theory is measured quantitatively by the contact angle for the system solid-water-oil, but in practice this quantity is extremely difficult to determine.

Slobod and Blum gave a semi-quantitative method for measuring the wettability of a reservoir rock. According to their method, the wettability of a rock specimen is determined by carrying out two displacement experiments, the first being the displacement of water by oil; the second the displacement of oil by air. They used the threshold (initial desaturation) pressures determined from the displacement experiments to calculate a "wettability number" W , which they defined as follows:

$$W = \frac{\cos \theta_{ow}}{\cos \theta_{oa}} = \frac{P_{(ow)T} \sigma_{ao}}{P_{(ao)T} \sigma_{wo}} \quad (1)$$

where $P_{(ow)T}$ = Threshold pressure for displacement
of water by oil

$P_{(oa)T}$ = Threshold pressure for displacement
of oil by air.

σ_{ow} = Contact angle in water for oil-
water-solid system

σ_{ao} = contact angle in oil for air-oil-
solid system.

They also defined an "apparent contact angle" the cosine of which is given by the relation

$$\cos(\theta_{ow})_{\text{apparent}} = \frac{P(ow)T \sigma_{ao}}{P(ao)T \sigma_{ow}}$$

which may be calculated if the assumption is made that the contact angle is zero in the oil for the air-oil-solid system. This calculation then yields the receding contact angle measured in the water phase.

As the "apparent contact angle" measurements were obtained for the system under static conditions, therefore their significance may be largely artificial, if used to define the wettability characteristics of the rock under dynamic conditions.

Bethel and Calhoun¹ surface treated glass beads with Dri-film to render them oil wet to n-octane to varying degrees, and determined the capillary desaturation curves by the restored state method. Their desaturation curves show a regularity of increasing displacement pressures as the oil wetness increases. The above desaturation curves were used to compute apparent contact angles between n-octane and water on glass. The family of desaturation curves they obtained, also shows a regular cross-over, such that the residual wetting liquid saturation values are in reverse order to the displacement pressures. Their results show a semi-logarithmic variation between the apparent contact angles and the residual saturation. From their desaturation data they interpreted that the wetting liquid ceases to be a continuous phase within individual pores before the capillary pressure can be raised sufficiently to force out the wetting phase completely. They also found out that the saturation of

wetting liquid at which the break in liquid continuity occurs is higher as the oil wetness decreases.

14

Newcombe, McGhee, and Rzasa developed a procedure for treating silica sand with a silicone polymer to produce surfaces of varying wettability. The wettability was evaluated by measuring the contact angle on a flat silica plate. Both the plate and the sand were treated simultaneously. The silica plate was placed in a rectangular optical cell and allowed to stand over-night under oil. The advancing silica-water-oil contact angle was formed by placing small drops, about 2 to 4 mm. in diameter, of the displacing phase on the silica plate. An enlarged image of the solid and drop was projected on to a screen, and the angle between the solid and the water-oil interface measured with a protractor from this image. They measured the contact angles at two to five minutes, at 30 minutes, at one hour and at 24 hours after the formation of the drop.

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Wagner and Leach, also followed a similar procedure of measuring contact angles. They made contact angle measurements on mineral surfaces using several sets of reservoir oil and water samples. Measurements with water and oil from sandstone reservoirs were made on polished quartz surfaces. Those for limestone reservoirs were measured on polished calcite surfaces.

7

Fatt and Brown gave a method for determining the fraction of preferentially oil wet and preferentially water wet area by nuclear magnetic relaxation measurements. The use of nuclear magnetic relaxation methods to measure fractional wettability is based on the observation that the surfaces of porous media contribute greatly to the relaxation rate of the fluids in the pores. Fatt and Brown observed, that in the case of

water-saturated sand packs the contribution of the surface to the relaxation rate of water in the pores is much less pronounced if the sand is Dri-filmed to make it preferentially oil wet. They measured the relaxation rate on five sand packs, containing 0, 25, 50, 75, and 100 percent Dri-film treated sand. They observed a linear relationship between nuclear magnetic relaxation rate of water and fractional preferentially oil wet surface area in a mixture of preferentially oil wet and preferentially water wet sand. They proposed to use this relationship to determine the fractional oil-wet surface area in natural rocks, with the help of a calibration curve obtained on sand packs of same size.

¹⁰
Holbrook and Bernard developed a method of determining relative water wettability (fraction of surface wet with water) of porous media, which involves the adsorption of methylene blue dye from an aqueous solution on to the solid surface of rock contacted by the injected dye solution. They found that water wet sand adsorbed a larger amount of dye from the solution. In the case of oil wet sand, the injected aqueous dye solution is prevented from contacting the adsorption surfaces by a film of oil, and virtually no dye is adsorbed. From experiments performed on mixtures of water wet and oil-wet sands, they found that relative water wettability could be determined with high degree of accuracy. One of the advantages of this method is that field cores can be tested as received without extraction or other handling that might alter their natural wettability.

²
Bobek, Mattax and Denekas, found that measurement of the rate and volume of spontaneous imbibition of the wetting phase by a rock is a reliable and reproducible test for a semi-quantitative determination of preferential

rock wettability. Their laboratory tests showed that the wettability of reservoir rock may depend on both the crude oil compositions and the rock type. They also found that coring fluids and core handling techniques can cause significant changes in the wettability of rock surfaces. They developed core handling and packing procedures which preserved core wettability during storage and laboratory testing. They then studied the comparative wettabilities of six water wet cores of natural sandstones and limestones, by a volumetric imbibition apparatus designed by Slobod and Moore, and found their method quite effective in determining the wetting condition of the cores.

LABORATORY FLOOD EXPERIMENTS

14

Newcombe, McGhee and Rzasa, performed water floods on laboratory unconsolidated sand models to study the effects of the solid-water contact angle and the oil water interfacial tension on oil recovery. They also studied the effect of water injection rate, and oil-water viscosity ratio on oil recovery for different wetting conditions of the porous medium. Advancing contact angles for water, in their experimental study ranged from 35° to 160° , and interfacial tensions from 1.2 to 44 dynes/cm. They varied the water injection rate from 1.2 to 400 cc/hr. and oilwater viscosity ratios from 1.46 to 296. They used sand models 59 in. long, 2.52 in. I.D. with average porosity of 33.5% and average permeability of 11 darcies.

They found that in both oil-wet and water wet systems and a low viscosity oil recoveries were functions of the oil-water interfacial tension; also an increase in flood rate resulted in increased oil recoveries. Higher

interfacial tension floods were more efficient than low interfacial tension floods on water wet systems, ($\theta < 90^\circ$) while low interfacial tension floods were more efficient on oil wet systems, ($\theta > 90^\circ$). They also found that intermediate or neutral wettability systems were less sensitive to rate of flood advance and interfacial tension, than either oil or water wet systems.

¹¹ Kennedy and Guerrero studied the effect of change in the surface and interfacial tensions of crude oil and water on oil recovery in Woodbine sand. They changed the surface and interfacial tensions of East Texas brine and crude oil by adding surface active agents to either of them. They found that lowering the interfacial tension had a tendency towards reducing the recovery of oil and that reduction of surface tension of the brine had little or no effect.

In their results as mentioned above, they excluded the results obtained from the runs in which they found that surface active additives had a tendency to make the sand less water wet or more oil wet. Hence the above results were essentially obtained on water wet systems. They also found that surface active agents that changed the wettability of sand from water wet to oil wet reduced the recovery of oil by water flooding as much as 8 percent.

¹²⁰ Wagner and Leach showed that oil displacement efficiency in water floods could be improved by wettability adjustment.

They carried out displacement tests, under water wet conditions, under oil wet conditions, and under conditions in which the wettability was completely reversed during the flood (from oil wet to water wet).

These latter tests were called wettability reversal floods. This was accomplished by adding 0.025 N HCl (pH = 1.6) or 50,000 ppm NaCl to flood water. They found out experimentally that increased oil recoveries could be obtained by reversing the wettability of the porous material from oil wet to water wet, during a waterflood, than either in the case of a water wet or oil wet system. This increase in oil recovery was about 7 to 8 percent pore volume over that attained in the conventional water floods in which no wetting change occurred. For their systems they also observed, that the higher the oil viscosity, the greater the percentage improvement obtained over conventional water flood recovery.

21

Warren and Calhoun made a study of water flood efficiency on short, consolidated Pyrex glass cores, rendered oil wet by chemical treatment. The variables they studied were the contact angle, interfacial tension, permeability and porosity, which they grouped into a single dimensionless group

$$\frac{C \cos \theta \sqrt{\frac{K}{\phi}}}{C V \mu_w L}$$

where C is the viscosity ratio held constant for all laboratory studies.

They also held the core length and velocity of flooding constant. They found that for a constant interfacial tension flood, for oil wet systems, breakthrough recoveries decreased linearly as the value of θ increased. Also for the floods for which $C \cos \theta$ was held constant, a linear decrease in breakthrough recoveries was observed as the interfacial tensions increased.

9

Haan studied the effect of capillary forces on the water drive process by means of linear displacement experiments in which the rate of injection, the oil water viscosity ratio and the wetting conditions of

the porous medium were varied. He carried out some of his experiments in transparent systems, which permitted the observation of fluid distribution. His floods were carried out at oil water density ratio of 1, in order to eliminate the influence of gravity. He observed that at low displacement rates capillary forces cause the formation of immobile pockets—even in relatively homogenous packs—resulting in low recoveries. With increasing rates the size of these pockets decreases, and recoveries increase accordingly. If the displacement rate is further increased, recoveries decrease again—provided that oil water viscosity ratio is larger than unity—owing to viscous fingering. As soon as the number of fingers becomes sufficiently large, recoveries are no longer dependent on rate.

¹³
Mungan performed laboratory water floods on oil wet and water wet alundum and Torpedo cores to study the effect of wettability and interfacial tension on oil recovery. The interfacial tensions and contact angles were changed by the addition of n-hexylamine to the flood water. He found that reduction of interfacial tension or transient change in core wettability recovered more oil than conventional floods. However, less additional oil was obtained from reversing the wettability of an initially oil wet core during a water flood than from lowering the interfacial tension with the core remaining oil wet throughout the flood.

His experimental results showed core wettability to be an important factor which controlled the amount of additional oil recovery by interfacial

tension reduction. Lowering the interfacial tension to the same value yielded greater additional recovery, if the displaced fluid was the wetting phase rather than the non-wetting phase.

APPARATUS AND EXPERIMENTAL PROCEDURE

The displacements were carried out in a stainless steel cell 38.35 inches long and 1.927 inches in internal diameter. This cell was packed in air, with glass spheres 61--104 microns in size. Before packing, the glass spheres were treated with hot chromic acid, washed with distilled water, and air dried at a temperature of 150°F. During the process of packing the cell was tapped with a mallet. In this way a random pack of 37.3 percent porosity was obtained. The steel cell was provided with end pieces. The inner faces of these end pieces had concentric and radial grooves cut into them so that the fluids entered or left the porous pack along the entire cross section of the latter, instead of at one point in the centre. Steel wire-mesh screens were used at both ends of the cell to prevent the glass spheres from leaving the cell. The cell was mounted horizontally in a large, double-walled wooden cabinet where the temperature was maintained at 100°F ($\pm 1^{\circ}\text{F}$).

A Ruska proportioning pump was used to deliver the flood water at a constant rate. A back pressure of about 60 psig. was maintained during all the floods, by means of a back pressure valve.

1. MEASUREMENT of POROSITY and PERMEABILITY

The core was evacuated to a pressure of 0.5 mm. of mercury, and then saturated with water. Several pore volumes of water were passed through it at a constant rate of 1200 cc./hr. The pressure drop across the

two ends of the core was measured and the permeability calculated by the Darcy's law. The porosity was determined by weighing the core before and after saturating it with water. The porosity and permeability values thus obtained are listed in Table 1.

2. WATER-FLOOD 1

The core was flushed with air and evacuated to a pressure of 0.5 mm. of mercury. As this pressure is lower than the vapour pressure of water at 100°F, a completely dry pack was assured.

The core was then saturated with Bayol--35 . This oil was kept in contact with the pack for 168 minutes, before the water flood was initiated. During this time a slow rate of flow of oil (60 cc./hr.) was maintained in the core. The water flood was carried out at a constant rate of 600 cc./hr. Break through recovery (when the first drop of water appeared in the effluent stream) was recorded and the flood continued till a water-to-oil ratio of 100 was obtained in the outflowing stream. These break through and ultimate recoveries are listed in Table 3.

3. WATER FLOOD 2

The core was flushed with air and washed with six pore volumes of iso-propanol. It was again flushed with air and evacuated. One pore volume of solution of 0.00125 per cent Dri-film, in benzene was then introduced into the cell. The cell was heated by means of an electric heating tape wound round it, until the temperature of the outer wall was about 150°F. The cell was rotated round its axis, in the horizontal position during the heating process. The benzene vapour coming out at

both ends of the cell was condensed and collected. After all the benzene in the cell had been distilled off, the cell was cooled and evacuated. It was then saturated with oil. The time taken from the beginning of the process of treating the pack with Dri-film until it was saturated with oil was 16 hours. The oil itself was kept in contact with the pack for 168 minutes before the water flood was started, as in Flood 1. Break through and subsequent productions were recorded and have been listed in Table 4.

4. WATER FLOODS 3, 4, and 5

These water floods were carried out in the same manner as Flood 2. After washing the pack with iso-propanol and evacuating it, the pack was treated with 0.00125 per cent, 0.05 per cent and 1 per cent solutions of Dri-film in benzene for floods 3, 4, and 5 respectively. The periods of time involved for each process were kept the same as in Flood 2. The production histories of these floods have been recorded in Tables 5, 6, and 7.

5. MEASUREMENT of INTERFACIAL TENSIONS

Interfacial tensions between water and oil were measured before and after these fluids passed through the porous medium. These interfacial tensions were measured by means of a duNuoy Tensiometer at 100°F, and have been listed in Table 9.

6. MEASUREMENT of CONTACT ANGLES

Contact angle measurements were carried out in thick walled glass capillary tubes, about 8 inches long and 0.025 inch in diameter. These tubes were treated with hot chromic acid, washed with distilled water, and dried in air at 150°F. They were then kept in contact with oil for a

period of about 168 minutes, after which they were lowered down vertically in a glass cylinder containing oil and water, and were kept suspended there with the upper end completely submerged in oil. This procedure assured that the contact angles so measured were the "advancing contact angles" for water. The distances between oil water interfaces, inside and outside the capillary tubes were measured by means of a travelling microscope, after the equilibrium was obtained. Equilibrium was considered to have been obtained when no perceptible movement of the menisci took place inside the capillary tubes over a period of one hour. These tubes were then repeatedly washed with iso-propanol, dried in air at 150°F, and treated successively with measured amounts of solutions (of known strengths) of Dri-film in benzene, and dried again in air at 150°F. Before every treatment with Dri-film, these tubes were repeatedly washed with iso-propanol and dried at 150°F. The heights (or depressions) of the water columns inside the capillary tubes above (or below) the water oil interface outside the capillary tubes, were measured corresponding to each of the treatments given above, when these tubes were suspended in cylinders containing water and oil, after having been kept in oil for 168 minutes. The strengths of the various solutions together with the heights (or depressions) of the water column have been listed in Table 10.

To determine the average radius of each of the capillary tubes, the length of a column of mercury of known weight, was measured inside the tube, and the radius calculated from a knowledge of the density of mercury.

From a knowledge of the interfacial tension between water and oil, the contact angles were calculated by the use of the following equation

$$\cos \Theta = \frac{h.r. \Delta \rho}{2 \sigma} g.$$

and have been recorded in Table 10.

To determine the accuracy of the above mentioned method, under the prevailing laboratory conditions, the angle of contact between water and glass (previously wetted with water) was measured against air. This measurement has been listed in Table 11.

7. IMBIBITION TESTS

The imbibition tests were carried out in an imbibition cell similar in construction to the one described by Bobek and Slobod and Moore.¹⁸ The glass spheres were packed in a lucite cylinder two inches long and one inch in internal diameter, and provided with wire mesh screens at both ends. This packed cylinder was then saturated with the non-wetting liquid. The pore volume was determined by weighing this cell before and after saturating it with the non-wetting liquid. The total time the glass spheres remained in contact with the saturating liquid was noted for all experiments. This lucite cylinder was placed in the imbibition cell, which was then filled with the imbibing liquid. Volumetric rates of imbibition were observed and have been recorded in Tables 12 to 16.

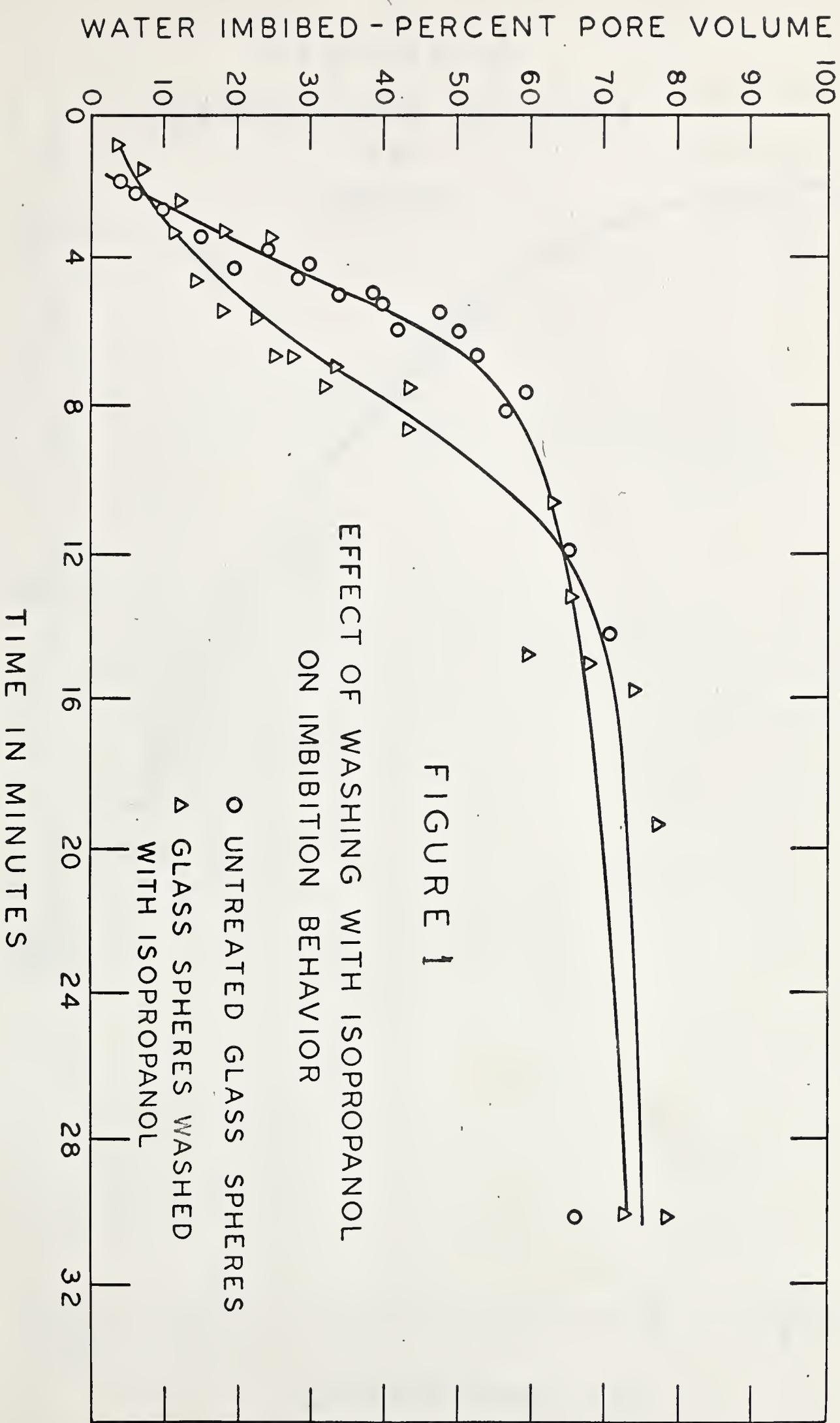
DISCUSSION OF EXPERIMENTAL PROCEDURE AND RESULTS

Iso-proponal was chosen as the washing liquid because of its complete miscibility, both in water and oil. In addition, over a certain range of concentrations there exists complete miscibility between all three phases. Iso-proponal has a relatively high vapour pressure at room temperature (40 mm. of mercury at 75° F) thus making it readily extractable from the core. As the core was always evacuated to a pressure lower than 0.5 mm. of mercury, complete removal of iso-proponal from the system was assured.

To find out if the original wetting conditions of the glass spheres could be reproduced, imbibition tests were run before and after washing with iso-proponal. Imbibition curves obtained from these tests are shown in Figure 1. As the two curves are quite close together, it was assumed that original wetting conditions could be restored after the core had been washed with iso-proponal and dried. The fact that the break through recoveries were reproducible to less than 1 per cent in the first flood also indicates that the original wetting conditions were restored after the pack was washed with iso-propanol.

TREATMENT of CORE WITH DRI-FILM

A series of preliminary tests were made to determine qualitatively the concentration of Dri-film SC-87, required to effectively cover the range from completely water wet to completely oil wet systems. These tests consisted of running imbibition curves on glass beads treated with Dri-film solutions of various strengths. Also glass capillary tubes were treated with these various solutions and a rough estimate of their wetting condition was

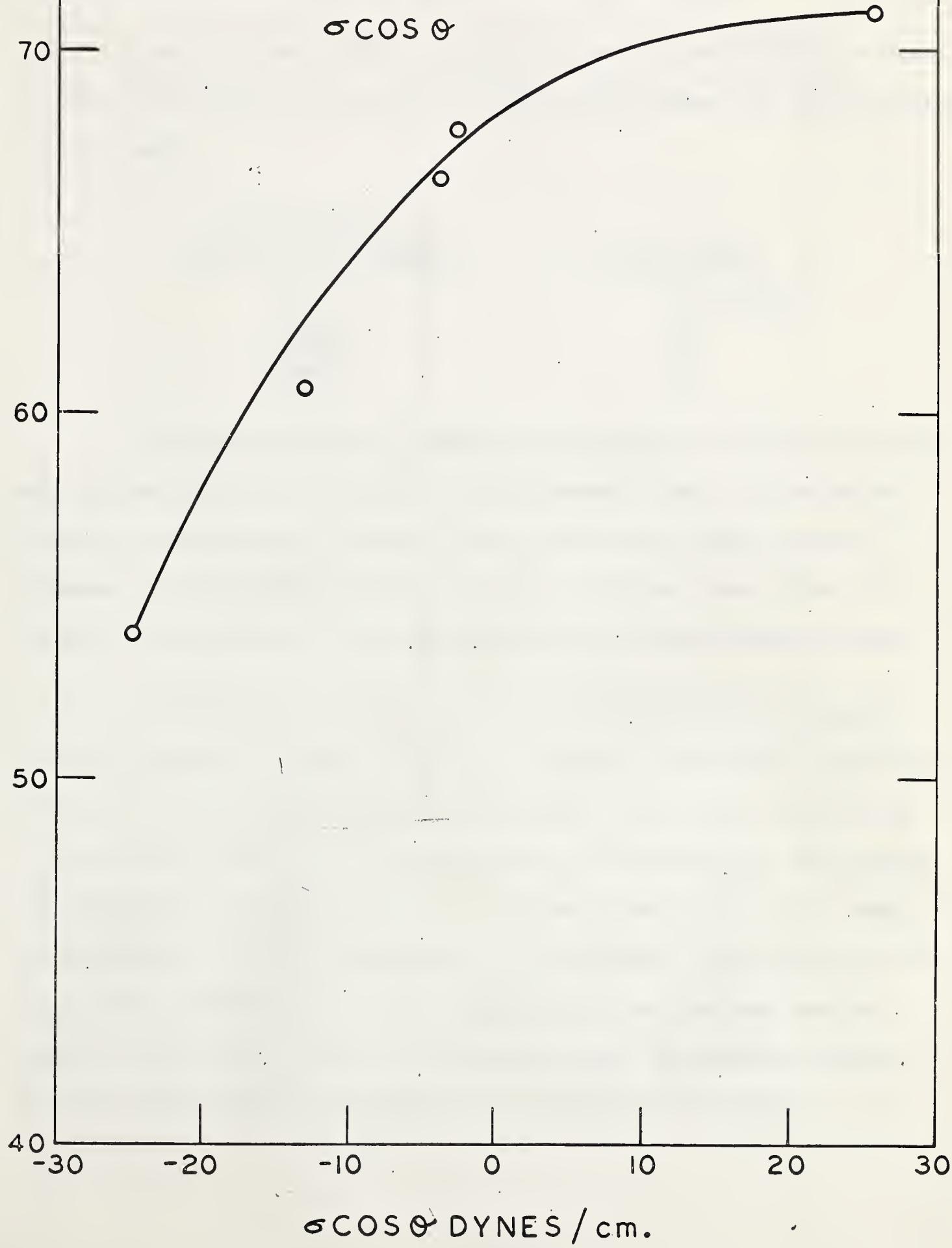


BREAKTHROUGH RECOVERY - PERCENT PORE VOLUME

FIGURE 2

BREAKTHROUGH RECOVERY

VS
 $\sigma \cos \theta$



made. This was done by observing whether the water column rose up or was depressed down--relative to the interface outside the capillaries.

The table below shows the concentrations of the Dri-film solutions in benzene selected on the basis of the above study along with the corresponding contact angles.

<u>Concentration</u> <u>(% Dri-film by volume)</u>	<u>Contact Angle</u>
.0	54 degrees
0.00125	93
0.00250	96
0.0525	104
1.0525	125

The glass equipment in which these solutions were made was treated with one per cent solution of Dri-film in benzene. This solution was kept in contact with the glass containers for several days, after which the glassware was repeatedly washed with benzene. This was done so that the strength of the dilute silicone solutions would not change during storage.

The approximate surface area per unit bulk volume of the porous pack was calculated as shown in Table 8. From this, the surface area treated by 1cc. of the Dri-film solution was calculated. The inside surface areas of the capillary tubes were also determined, and the volume of the treating liquid required, to correspond to the treatment given to the porous medium was established. As this volume was found to be small, the treating liquid was diluted several fold, so that a comparatively uniform layer was deposited on the inside surface of a capillary tube. The required volume of the treating liquid was measured in the capillary tube itself.

It might be expected that in the process of drying the pack, as the benzene vapour leaves the system, the more concentrated treating liquid will have a tendency to collect around the grain contact points in the form of pendular rings. Also by the same reasoning this liquid may have a tendency to collect in pores which are smaller in size. If this reasoning holds true, then within the porous pack, we might have certain points which are comparatively much more oil wet (or less water wet) than the rest of the core. Also this may give rise to high permeable, relatively more water wet channels, in which water could flow more freely than in the rest of the core.

On the other hand the spreading coefficients of the silicones are very high. There is a great tendency on the part of the silicones to attach themselves to glass surfaces. As the concentrations of the Dri-film solutions were low, the possibility of the silicones being uniformly distributed on the entire glass surface area available, is quite high. The total time involved in the treatment of the porous pack with Dri-film was 16 hours. It has been assumed that during this period of time, a porous pack of uniform wettability was obtained.

It should be pointed out that in the treatment of capillary tubes by the silicone fluid, it is possible that the distribution of the silicones was not uniform on the entire surface area involved. Thus it is quite possible that certain parts of the capillary tubes were more oil wet than others. For this reason, the contact angle measurements were made on three capillary tubes simultaneously, and an average value of the contact angle was established from this data.

INTERFACIAL TENSIONS

The correction due to the weight of the liquid clinging to the lower part of the ring was applied to all interfacial tension readings. The maximum difference in the water oil interfacial tension at the outlet end and at the inlet end was 7 per cent, the average difference being 4 per cent. This reduction in the interfacial tension between water and oil may be due to the presence of small amounts of hydrochloric acid in the effluent water. This hydrochloric acid will be produced by the hydrolysis of unreacted methyl-chlorosilane present in Dri-film. The water oil interfacial tension at the outlet end was always lower than at the inlet end. An average value of the interfacial tensions was used in evaluating $\sigma \cos \theta$.

IMBIBITION TESTS

Reproducible imbibition tests could only be obtained if the time for which the porous pack containing the non-wetting liquid remained in contact with air, was held constant. This period is the time taken in transferring the core from the saturating vessel to the imbibition cell, and weighing it. A water wet pack saturated with oil will have a tendency to absorb moisture from atmosphere thus reducing the capillary pressure available for the displacement of oil by water. The above reasoning will also apply if the glass spheres were contaminated with moisture, before being saturated with the non-wetting liquid. Due to this reduction in the displacement pressure, the time taken for the first drop of water to be imbibed was much longer than if the core was kept moisture-free before being placed in the imbibition cell.

In figure 5, imbibition tests made on two cores consisting of

FIGURE 3
RECOVERY
VS.
WATER INJECTION

RECOVERY - PERCENT PORE VOLUME

100

75

50

25

0

- $\sigma \cos \theta = 25.9$
- △ $\sigma \cos \theta = -3.9$
- $\sigma \cos \theta = -10.46$
- $\sigma \cos \theta = -24.7$

2

3

4

5

6

PORE VOLUMES FLOOD WATER INJECTED



water wet glass spheres have been compared. One core had remained in contact with oil for 200 minutes. The other core had remained in oil for 13 hours. The imbibition behaviour of these cores is substantially the same, thus showing that the time the glass spheres remained in contact with oil, did not seem to effect the imbibition behaviour of the pack.

RESULTS of WATER FLOODS

Maximum and minimum break through recoveries of 70.8 and 54.0 per cent of total pore volume were obtained in the most water wet and in the most oil wet systems, respectively. The break through recoveries for the intermediate wettability conditions lay between these two extreme values (Figure 2).

The ultimate recoveries, i.e., the recoveries up to the point when the W. O. R. in the effluent stream is greater than 100, have also been found to be maximum for the water wet system and minimum for the oil wet system (See Figure 3). These results are in good agreement with the theory developed earlier, and also compare favourably with the published results of similar studies made by Newcomb et al,¹⁴ and several other.

Water flood efficiencies can best be discussed, if break through and ultimate recoveries are studied as function of $\cos \theta$. For the system under study the break through recovery decreased from 70.8 per cent to 54 per cent as θ increased from 54° to 125° degrees, the water oil interfacial tension remaining constant at 44 dynes/cm. The

BREAKTHROUGH RECOVERY - PERCENT PORE VOLUME

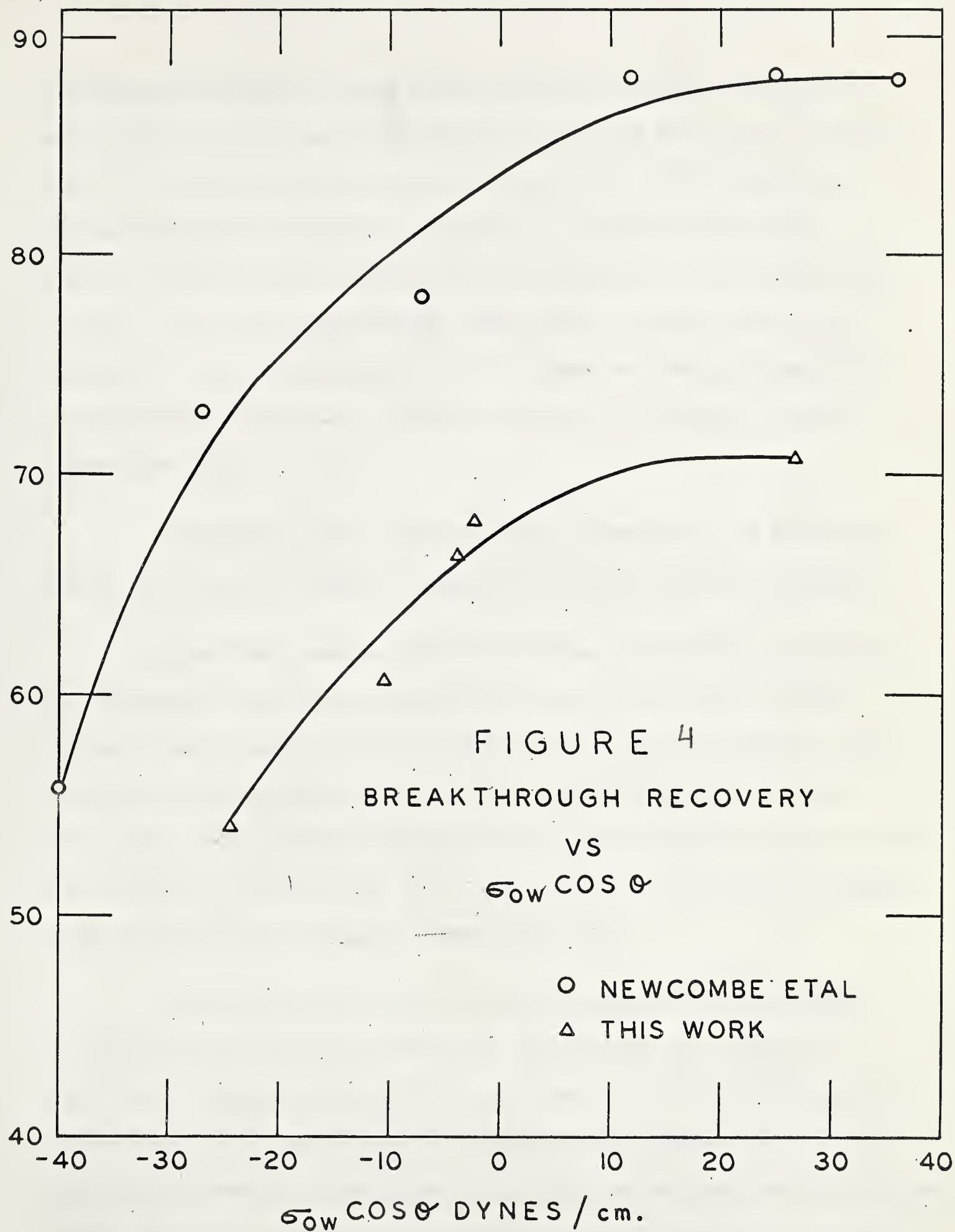
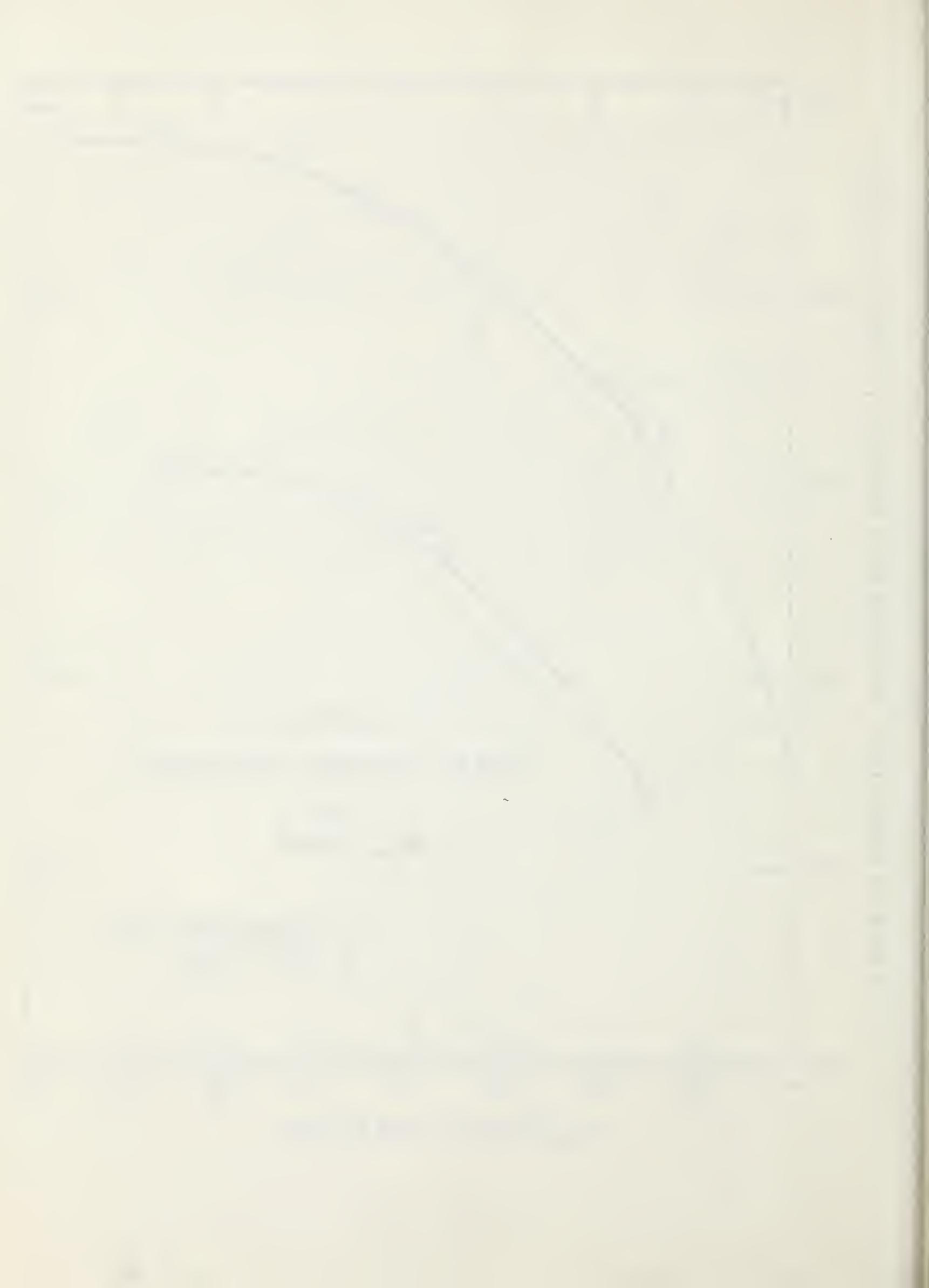


FIGURE 4
BREAKTHROUGH RECOVERY
VS
 $\sigma_{ow} \cos \theta$

○ NEWCOMBE ET AL.
△ THIS WORK

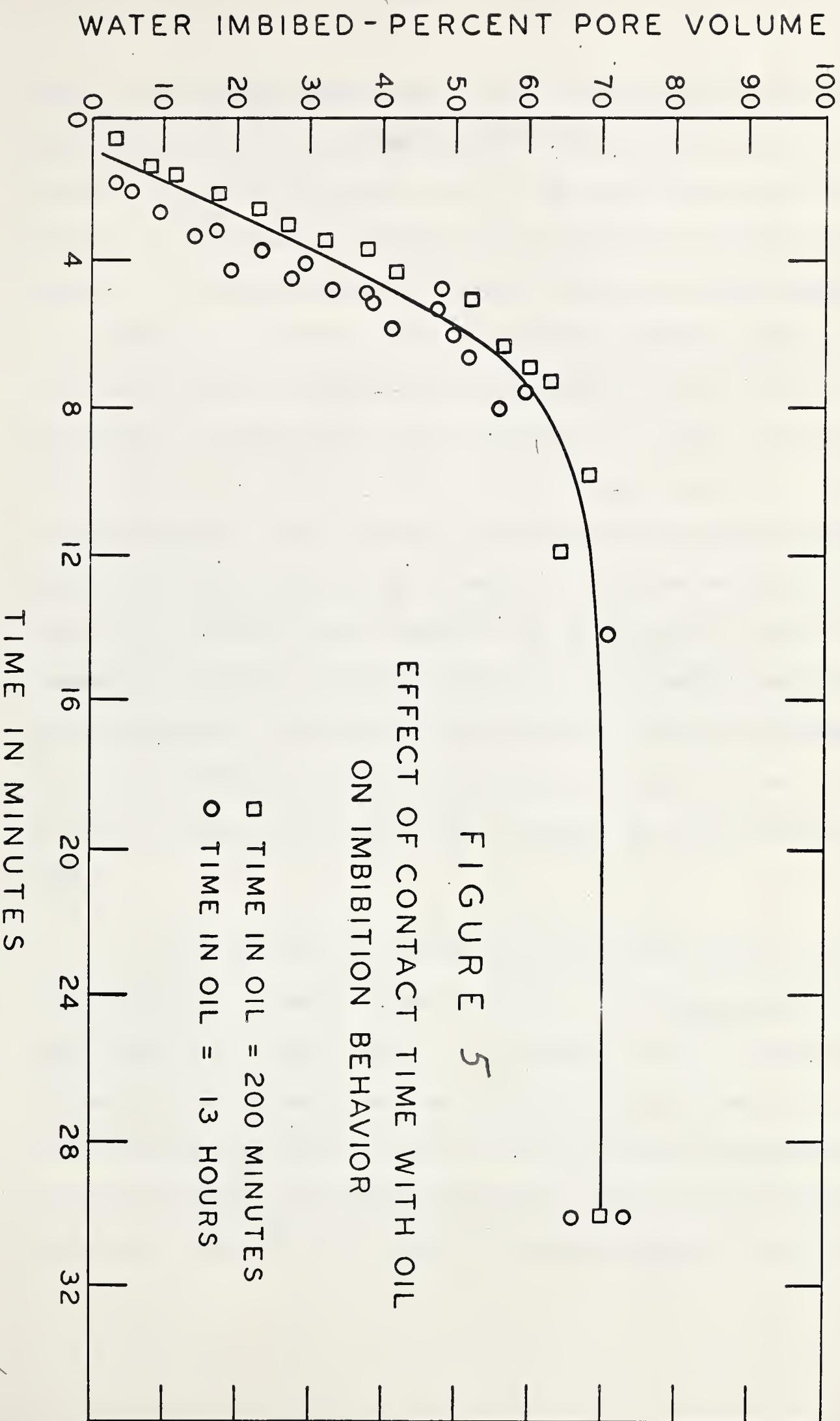


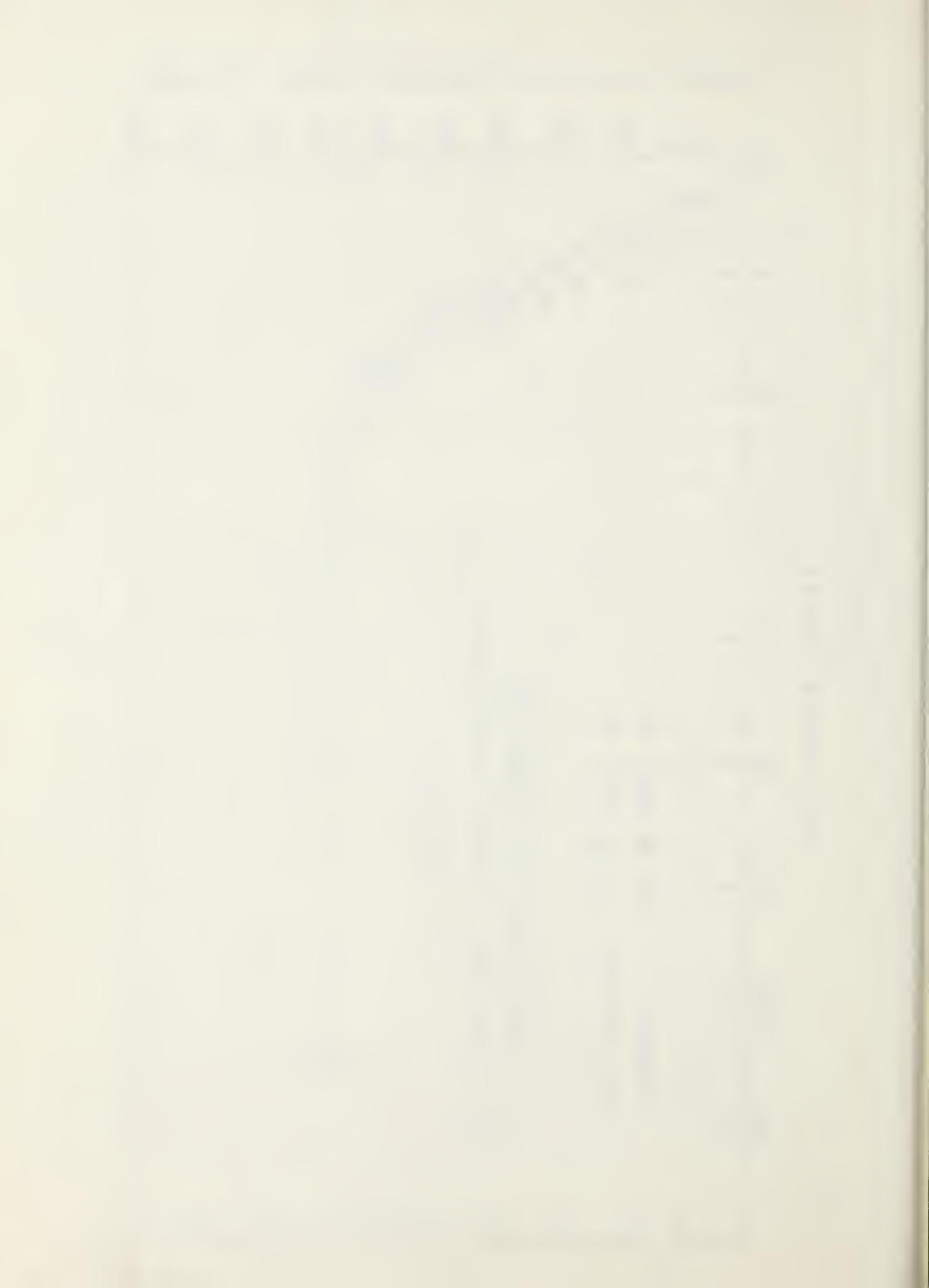
corresponding decrease in break through recovery for low viscosity ratio water floods, in the case of Newcombe et al was from 80 per cent to 58 per cent, as θ increased from an average value of 35° to 155° (interfacial tension remaining constant at 44 dynes/cm.) A similar trend is also observed for the ultimate recovery which decreased from 95 per cent to 75 per cent. The higher break through and ultimate recoveries obtained by Newcombe et al are probably due to the fact that the average permeability of their porous systems was 11 darcies compared to 2.1 darcies for the system under study.

The results of this work and those of Newcombe et al have been plotted as function of $6\cos\theta$ in Figure 4 for the purpose of comparison.

Water flood results obtained by Warren and Calhoun on short oil wet Pyrex glass cores show a decrease of 11 per cent in break through recovery, when interfacial tension increased from 10 to 55 dynes/cm. the contact angle remaining constant. Their constant interfacial tension water floods show a decrease of about 20 per cent in break through recovery with a change in the value of $\cos\theta$ from -0.90 to -0.99, which corresponds to an increase in the value of θ from 119° to 159° .

The slope of oil recovery vs water injection curve in Figure 3 is greater for the oil wet systems than for the water wet systems. In other words, the producing W. O. R. at any instant is higher for water wet systems than for oil wet systems. To explain this phenomenon it must be realized that even in an idealized porous pack, the cavities and constrictions are not all of the same size, but might show a size distribution of finite

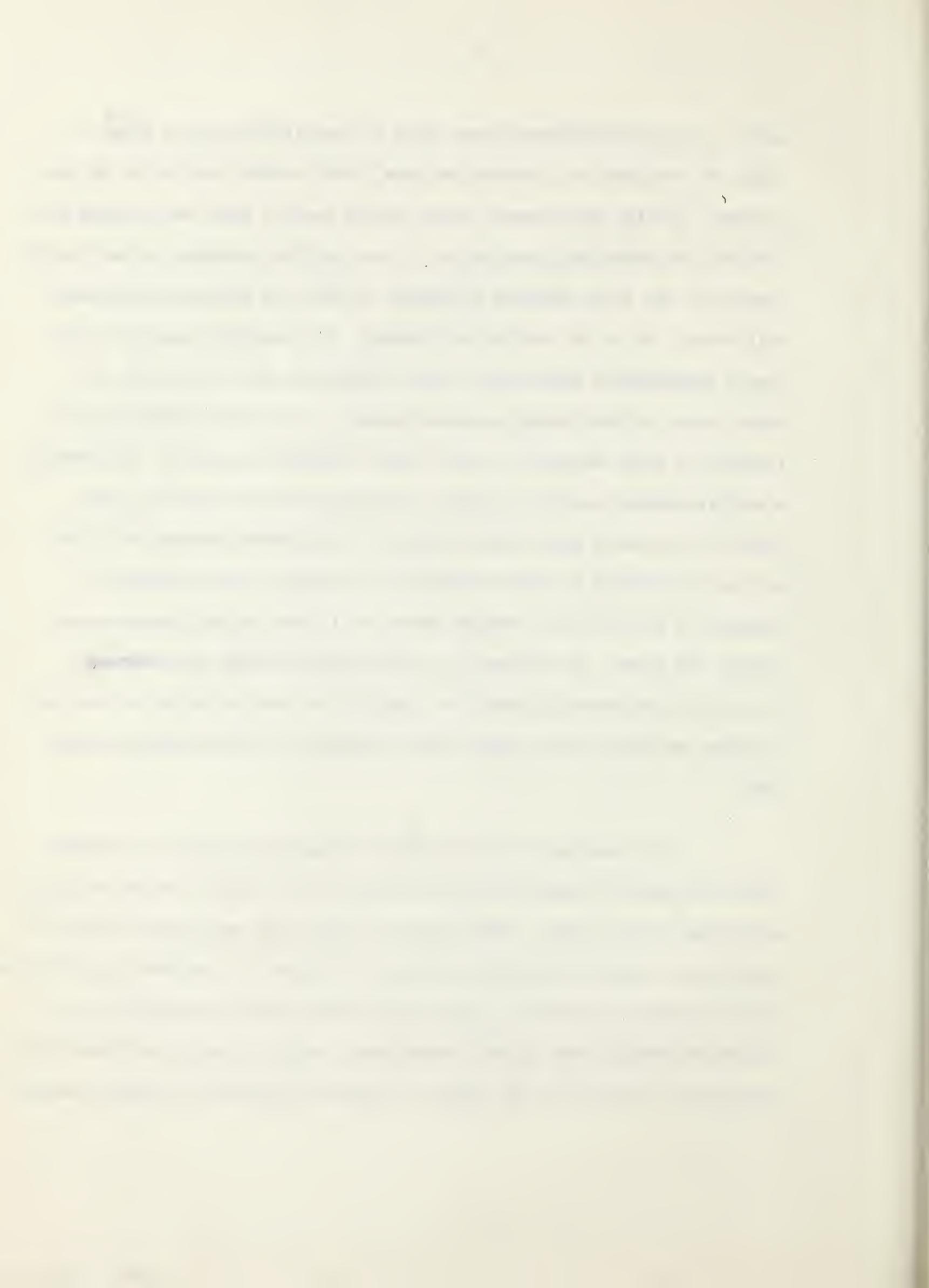




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width. At low displacement rates, such a size distribution is known to cause the formation of a transition zone, both in water wet and in oil wet systems. At high displacement rates, in the case of water wet systems this zone will be practically negligible if the capillary pressure is small with respect to the total pressure difference so that the frontal displacement will occur. In an oil wet system, however, the transition zone may still have a considerable length under these conditions, due to the fact that water tends to flow through separate channels. The wider channels will be favoured by water because of their smaller viscous resistance. Consequently a zone is formed in which the water saturation varies gradually, which results in an early water break through. As discussed earlier, if in the process of treating the pack with Dri-film solution, the latter had a tendency to accumulate in smaller pores, or in the smaller constrictions between the pores, the chances of an early break through are enhanced. In this case the wider channels are likely to be more water wet or less oil wet than the rest of the system, thus favouring the flow of water through them.

It is realised that the method of measuring angles in capillary tubes only gives a semi-quantitative measure of the contact angles actually prevailing in the system. These contact angles have been measured for the system under static conditions, and from this point of view their significance may be largely artificial if used to define wettability characteristics of the porous medium under dynamic conditions. Again as Cassie and Baxter⁴ have pointed out, that due to the effect of surface roughness, the contact angles



prevailing in the porous system will be different from the contact angles measured on the relatively smooth walls of capillary tubes.



CONCLUSION

1. A procedure has been developed for treating a porous pack consisting of glass spheres with Dri-film solutions of increasing concentrations to render it more oil wet.
2. A method has been suggested for quantitatively estimating the wetting conditions of a pack of glass spheres. This consisted of applying a coating of Dri-film of the same density as the pack, to the interior surface of glass capillary tubes, and determining the contact angles from the capillary rise measurements. This technique has been found to be more convenient than those described in the prior literature.
3. The water flood results have shown that the break through recovery decreases from 70.8 per cent to 54 per cent as the estimated value of the contact angle for water prevailing in the system, increases from 54 degrees to 125 degrees. A similar trend is also shown by the ultimate recovery which decreases from 91 per cent to 80 per cent for the above change in the wetting conditions of the porous medium.

NOMENCLATURE

Subscripts o and w pertain to oil and water respectively

C	viscosity ratio, dimensionless
g	acceleration due to gravity, cm./sec. ²
h	height, cm.
J	Leveretts "J" function
K	absolute permeability, darcies
k_{ro} , k_{rw}	relative permeabilities, dimensionless
L	length, cm.
M	mobility ratio, dimensionless
Pc	capillary pressure, atmosphere
p	pressure, atmosphere
r	radius of the capillary tube, cm.
S	saturation, dimensionless
t	time, seconds
V	injection rate, cm./sec.
ϕ	porosity, dimensionless
σ	water oil interfacial tension, dynes/cm.
ρ	density, gm./cm. ³
π	flow potential, atmosphere
μ	viscosity, cp.
θ	water oil contact angle, degrees

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A P P E N D I X

TABLE ICORE PROPERTIES

POROSITY	37.3%
PERMEABILITY	2.1 darcies
LENGTH	38.35 inches
DIAMETER	1.926 inches

SIEVE ANALYSIS

U. S. Series Screen Mesh	Weight Percent
+ 100	0.5
-100 + 140	28.0
-140 + 200	53.0
-200 + 230	6.5
-230	<u>12.0</u>
	100.00

TABLE 2FLUID PROPERTIES1. WATER

	<u>TEMPERATURE</u>	
	75° F	100° F
Density	0.998 gm./cm. ³	0.993 gm./cm. ³
Viscosity	0.925 cp.	0.685 cp.
Surface Tension		
Observed	75.97 dynes/cm.	73.0 dynes/cm.
Corrected	71.0	68.5

2. BAYOL-35

Density	0.774 gm./cm. ³	0.765 gm./cm. ³
Viscosity		1.884 cp.
Surface Tension		
Observed	26.8 dynes/cm.	25.6 dynes/cm.
Corrected	24.0	23.2

3. WATER OIL INTERFACIAL TENSION

Observed	43.4 dynes/cm.	43.3 dynes/cm.
Corrected	45.0	44.9

TABLE 3PRODUCTION HISTORY - FLOOD I

Injection Rate = 600 cc/hr.

 S_0 = 100%

Core Treatment: Glass spheres treated with hot chromic acid and washed with distilled water (outside the core holder)

<u>Total Cum. Production</u>	<u>Cum. Oil Production</u>	<u>Cum. Water Production</u>	<u>Inst. W.O.R.</u>	<u>Oil Rec. In Pore Volumes</u>	<u>Water Inj. P.V.</u>
485	485	0	0.000	0.708	0.708
490	488	2	0.004	0.712	0.715
996	594	402	3.774	0.867	1.454
1481	624	857	15.160	0.911	2.162
2466	629	1837	196.000	0.918	3.60
3466	631	2835	489.000	0.921	5.06
4466	632	3834	999.000	0.922	6.52

TABLE 4PRODUCTION HISTORY - FLOOD 2

Injection Rate: 600 cc/hr. $s_0 = 100\%$

Core Treatment: 0.0125% Dri-film

<u>Total Cum. Production</u>	<u>Cum. Oil Production</u>	<u>Cum. Water Production</u>	<u>Inst. W.O.R.</u>	<u>Oil Rec. In P.V.</u>	<u>Water Inj. P.V.</u>
464	464	0	0.000	0.671	0.671
465	465	1	0.002	0.677	0.677
985	566	419	4.10	0.826	1.44
1485	591	894	19.00	0.863	2.17
2485	610	1875	49.00	0.891	3.63
3485	620	2865	99.00	0.905	5.09
4485	629	3856	125.00	0.917	6.55

TABLE 5PRODUCTION HISTORY - FLOOD 3

Injection Rate:

600 cc/hr.

 $S_0 = 100\%$

Core Treatment:

0.0025% Dri-film

<u>Total Cum. Production</u>	<u>Cum. Oil Production</u>	<u>Cum. Water Production</u>	<u>Inst. W.O.R.</u>	<u>Oil Recovery P.V.</u>	<u>Water Inj. P.V.</u>
455	455	0	0.00	0.664	0.664
457	455	2	0.004	0.664	0.667
977	555	422	4.20	0.810	1.426
1477	590	887	13.20	0.861	2.156
2477	606	1871	61.30	0.884	3.612
3477	618	2859	82.10	0.902	5.076
4477	624	3853	123.75	0.911	6.536

TABLE 6PRODUCTION HISTORY FLOOD 4

Injection Rate: 600 cc./hr. $s_0 = 100\%$

Core Treatment: 0.0525% Dri-film

<u>Total Cum. Production</u>	<u>Cum. Oil Production</u>	<u>Cum. Water Production</u>	<u>Inst. W.O.R.</u>	<u>Oil Rec. P.V.</u>	<u>Water Inj. P.V.</u>
415	415	0	0.00	0.605	0.605
988	526	462	2.51	0.768	1.442
1488	548	940	21.73	0.800	2.172
2478	563	1915	65.00	0.822	3.618
3484	568	2916	197.0	0.829	5.086
3984	570	3414	249.0	0.832	5.816

TABLE 7PRODUCTION HISTORY - FLOOD 5

Injection Rate: 600 cc/hr. $S_0 = 100\%$

Core Treatment: 1.0525% Dri-film

<u>Total Cum. Production</u>	<u>Cum. Oil Production</u>	<u>Cum. Water Production</u>	<u>Inst. W.O.R.</u>	<u>Oil Recovery P.V.</u>	<u>Water Inj. P.V.</u>
370	370	0	0	0.540	0.540
492	427	65	0.877	0.623	0.718
994	472	432	10.16	0.689	1.451
2014	507	1507	28.14	0.790	2.94
2989	517	2472	96.5	0.755	4.364
3509	527	2982	99.0	0.769	5.123
4509	537	3972	100.0	0.783	6.582
5509	547	4962	100.0	0.80	7.25

TABLE 8

Average diameter of the glass spheres	=	0.009 cm.
Surface area per unit volume of the porous pack	=	$\frac{4\pi r^2 (1-\phi)}{4/3 \pi r^3}$
	=	$\frac{3 \times 0.627}{0.0045}$
	=	418 cm. ²
Surface area treated by 1cc. of the treating solution	=	<u>418</u>
	=	$\frac{418}{0.37}$
Average radius of the capillary tubes	=	0.0032 cm.
Length of each capillary tube	=	20 cm.
Inside surface area of the capillary tubes	=	$2\pi r$
	=	$2 \times 3.142 \times 0.032 \times 20$
	=	4.02 cm. ²
Volume of the treating liquid required	=	$3.577 \times 10^{-3} \text{ cm.}^3$
Area of cross section of each capillary tube	=	πr^2
	=	$3.142 \times (.032)^2$
	=	.00332 cm. ²
The required length of the liquid column in the capillary tube to correspond to the treatment given to the porous pack	=	$\frac{0.0036}{0.0032}$
	=	1.08 cm.
Length of the actual column taken	=	20 cm.
The extent to which the treating solution was diluted	=	18.5 times by volume

TABLE 9

BREAK-THROUGH RECOVERY AS A FUNCTION OF WETTABILITY

Flood No.	Treatment	B. T. Recovery in Per cent P. V.	Interfacial Tensions(σ) dynes/cm.			$\cos\theta$	$\sigma\cos\theta$
			Inlet Fluids	Outlet Fluids	Average		
1	Chromic Acid	70.8	45	44.1	44.5	0.5812	25.9
2	0.00125% Dri-film	67.7	45	44.8	44.9	-0.0597	-2.7
3	0.0025% Dri-film	66.4	45	44.1	44.5	-0.0886	-3.9
4	0.0525% Dri-film	60.6	45	42.6	43.8	-0.2389.	-10.46
5	1.0525% Dri-film	54.0	45	42.1	43.6	-0.5654	-24.7

TABLE 10

GLASS-WATER-OIL CONTACT ANGLE MEASUREMENTS

Average Radius of Capillary Tubes = 0.0329 cm.

Interfacial Tension between water and oil = 45.0 dynes/cm.

Flood No.	Treatment	Capillary Rise in cm.			$\cos \Theta$	Θ
		Tube 1	Tube 2	Tube 3		
1	Hot Chromic acid-washed	6.7	8	7.4	7.3	0.5812
2	0.00125% Dri-film	-0.50	-0.75	-1.0	-0.75	-0.0597
3	0.0025% Dri-film	-0.75	-1.7	-1.1	-1.2	-0.0886
4	0.0525% Dri-film	-3.7	-3	-2.5	-3.0	-0.2389
5	1.052% Dri-film	-6.0	-8.5	-7.0	-7.1	-0.5654

TABLE 11

MEASUREMENT OF CONTACT ANGLE BETWEEN
GLASS AND WATER AGAINST AIR

Rise of Water in the Capillary Tube	=	4.625 cm.
Radius of the Capillary Tube	=	0.0315
Interfacial Tension between Water and Air	=	70.5 dynes/cm.
Acceleration due to Gravity	=	981.15 cm./sec. ²
Density of Water	=	0.998 gm./cm. ³

Neglecting the density of Air,

$$\begin{aligned} \cos \theta &= \frac{L.r.g. \rho}{2\sigma} \\ &= \frac{4.625 \times 0.0315 \times 981.15}{2 \times 70.05} \\ &= 0.9989 \end{aligned}$$

Thence $\theta = 2^\circ 39'$

TABLE 12INBIBITION TEST I

Porous Medium:

Water wet glass spheres

Pore Volume:

10.55 cc.

Time in Oil:

200 minutes

Time in Air:

5.0 minutes

<u>Time In Minutes</u>	<u>Water Imbibed, CM³</u>	<u>Water Imbibed Percent Pore Volume</u>
1.9	0.4	3.8
2.6	1.0	9.5
3.3	1.5	14.4
4.2	2.0	19
9.9	3.0	28.5
9.7	3.5	33
5.1	4.1	39
5.3	5.0	47.5
5.9	5.3	50
6.3	5.9	56
7.5	6.3	59
11.9	6.8	69.5
30.0	6.9	66

TABLE 13IMBIBITION TEST 2

Porous Medium: Water Wet Glass Spheres

Pore Volume: 10.5 cc.

Time in Oil: 200 minutes

Time in Air: 5 minutes

<u>Time in Minutes</u>	<u>Water Imbibed, CM³</u>	<u>Water Imbibed, Percent Pore Volume</u>
2.1	0.5 cc.	5.74
3.2	1.5	17.2
3.7	2.0	23
4.0	2.5	29
4.8	3.3	38
5.8	4.0	41
6.6	4.5	52
8.0	4.9	56
14.0	6.1	70
30.0	6.4	73

TABLE 14IMBIBITION TEST 3

Porous Medium: Water Wet Glass Spheres
 Pore Volume: 8.5 cc.
 Time in Air: 5.0 minutes
 Time in Oil: 13 hours

<u>Time in Minutes</u>	<u>Water Imbibed, CM³</u>	<u>Water Imbibed, Percent Pore Volume</u>
0.6	0.3	3.5
1.5	0.7	8.2
1.7	1.0	11.7
2.1	1.5	17.7
2.6	2.0	23.4
3.0	2.3	27.0
3.4	2.7	32
3.7	3.2	38
4.3	3.6	42
4.7	4.1	48
5.0	4.4	52
6.2	4.8	56
6.8	5.1	60
7.2	5.4	63
9.9	5.8	68
30 minutes	6.0	70

TABLE 15IMBIBITION TEST 4

Porous Medium:	Water Wet Glass Spheres	
Pore Volume:	8.5 cc.	
Time in Oil:	200 minutes	
Time in Air:	5	
<u>Time in Minutes</u>	<u>Water Imbibed, CM³</u>	<u>Water Imbibed, Percent Pore Volume</u>
1.5	0.5	5.9
2.3	1.0	11.8
3.2	1.5	17.7
3.4	2.0	23.6
5.5	2.3	27.2
6.9	2.8	33.1
10.3	4.2	49.6
14.5	5.0	59.0
30.0	6.1	72.0

TABLE 16IMBIBITION TEST 5

Porous Medium: Water Wet Glass Spheres
 Pore Volume: 9.1 cc.
 Time in Oil: 200 minutes
 Time in Air: 5

<u>Time in Minutes</u>	<u>Water Imbibed, CM³</u>	<u>Water Imbibed, Percent Pore Volume</u>
0.8	0.3	3.3
1.5	0.5	5.5
2.4	0.8	8.8
3.2	1.1	11.1
4.5	1.3	14.1
5.3	1.6	17.6
5.5	2.0	22.0
6.5	2.5	25.0
7.4	3.5	32.0
8.5	4.0	43.5
10.5	5.6	61.5
13.1	5.9	65.0
13.9	6.9	67.5
15.6	6.7	73.0
19.3	7.0	77.0
30.0	7.1	78.0



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